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Modeling the effect of pigments and processing parameters in polymeric composite for printing ink application using the response surface methodology

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ABSTRACT

Digital printing is currently in high demand. Toner is a powder mainly composed of polymer and colorant that are used as ink in digital printing. The provision of a suitable color printing depends on appropriate selection of colorants and production parameter capable of producing a thin layer on paper. In this study, for the first time, the production of color printing toners (cyan, magenta and yellow) via emulsion aggregation method was optimized through response surface methodology with considering the effect of colorant. Evaluations were made for the influence of the colorant and production parameters on toner characteristics using particle size analysis, scanning electron microscopy (SEM), calorimetry and differential scanning calorimetry (DSC). The optimization involved two factors (time and agitation speed) and three responses (particle size (μm), particle size distribution and colorimetric properties (L^*, a^*, b^*) for each colorant. The response surface results demonstrated that each colorant due to its physicochemical properties showed different behavior. The results also showed that changing production conditions, such as increasing time or agitation rate, separately could not produce high-quality color printing toner. Therefore, an optimum condition was determined for each colorant. Results demonstrated that increasing the polarity of a pigment produced better dispersion and lower particle size with narrower distribution, while changing a pigment's characteristics did not affect the toner shape or its thermal properties.

1. Introduction

Digital printing is the latest generation of the publishing and printing industry, and electrophotographic (EP) printing is one of its key technologies. Toner, the ink for digital electrophotographic printing is a composite material based upon a polymer matrix within which the colorant (organic or inorganic pigment nanoparticles and/or dyes) is incorporated [1,2]. In recent years, color printers with high speed and high image quality have been commercially introduced and allow easy and fast printing. These features make such printers ideal for use in small or large-volume print jobs in the printing market [3]. Toner-based printing technologies can be divided into six steps: cleaning, conditioning, writing, developing, transferring, fusing [4]. For color printing, this six-step process is iterated four times for cyan, magenta, yellow, and black images, and the colors are overlapped. Manufacturers offer a complete range of high-quality raw materials for color printing toners [5,6]. Physical properties of the toner play a vital role in determining the quality of printing. In other words, toner color, circularity, size and size distribution are important factors in determining the printing machine's performance and the quality of the final printed image, especially for advanced high-resolution color printing [7]. Typically, toners possessing favored homogeneity, particle size and shape distribution can be produced through well-established emulsion aggregation (EA) methods, in which the final properties are precisely controlled [8,9]. EA is one of the newest, easily controlled and green chemical methods, allow fine-tuning of particle design, especially particle size, distribution, composition, structure, morphology and circularity [10,11]. The importance of this method is also because of being environmentally-friendly regarding both the process and resulting product. To optimize print quality, the goal is to create a small, spherical toner with a narrow distribution [12].

Colorants have always played a vital role in every medium they are used in, which includes coating, composite and ink [13,14]. Therefore, as expected, one critical and important toner

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components are colorant, which must be selected properly in order to satisfy coloristic requirements. Furthermore, colorants have a significant effect on toner properties like particle size and particle size distribution which affect print quality [15–17]. Therefore, it is important to investigate the effect of colorant and find the optimum condition for each colorant in the toner production process. In the previous study the authors' intention was to choose appropriate pigments and investigate ways in which the physicochemical, chemical constitution and solid-state parameters of organic pigments are responsible for physical characteristics of color printing toner produced by the EA method [15]. In this study, for the first time, the purpose of the study is to optimize production parameters for each colorant using response surface methodology (RSM).

2. Theory of response surface methodology (RSM)

RSM is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems, in which a response of interest is influenced by several variables and the objective is to optimize this response. The responding variable can be represented by contour plots, an array of digits or a function containing changing variables. This approach employs quantitative data from appropriate experiments to develop multivariate equations and solve them simultaneously. In general, two modes of approximating functions, namely first and second-order regression are employed for analyzing the variation behavior. In the case that study of interaction between changing variables is of vital importance, a second-order regression function gives a deeper understanding. This methodology provides too few unique design points compared to a full factorial design, therefore the quadratic function is well-known as the most popular class of RSM for fitting the experimental data. Despite the fact that cubic regression functions have rarely been applied to experimental data, when the responding variable is very sensitive to changing variables, the interaction between parameters is deemed to be of vital importance; a third-order model provides a broader understanding of process nature. This can be observed from the following equation:

$$\eta = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj}x_j^2 + \sum\sum_{i<j=2}^{k}\beta_{ij}x_i x_j + \sum_{i=1}^{k}\sum_{j\geq i}^{k}\sum_{k\geq j}^{k}\beta_{ijk}\chi_i\chi_j\chi_k \quad (1)$$

In this expression, the coefficient β_{ijk} takes the interaction coefficient between all variables into account. There are two ways to design the desired experiments based upon RSM, namely Box–Behnken design (BBD) and central composite design (CCD). The full CCD method includes factorial points from a full factorial (2^k), axial points, and center points. Application of the standard statistical method of analysis of variance (ANOVA) makes it possible to assess the reliability and the accuracy of experimental results analyzed by a cubic interpolation function [18,19].

3. Experimental methods and materials

3.1. Materials

The polymer used in this study was a styrene–acrylic resin (NS88; Simab Resin Co., Tehran, Iran) with a medium pH value. The polyethylene emulsion wax (Hydrocer EE 95, Shamrock Technologies, Inc., NJ, USA) and poly aluminum chloride was used as coagulation agents. The pigments used in this study were C.I. Pigment Blue 15:3 (P.B. 15:3) as the cyan colorant (BASF, Germany), C.I. Pigment Yellow 151 (P.Y. 151) as the yellow colorant (Clariant, Switzerland), C.I. Pigment Red 57:1 (P.R. 57:1) and C.I. Pigment Red 122 (P.R. 122) as the magenta colorants (Clariant, Switzerland). Scheme 1 illustrates the pigments structure.

Table 1
Factors and levels used in the factorial design and response surface.

Factors	Symbol	Unit	Level		
			−1	0	+1
Mixing time	T	h	2	5	8
Agitation speed	S	rpm	500	1250	2000

3.2. Color toner production procedure

Toner particles were produced via a stepwise procedure, in accordance with previous studies [4,12,15]. First, a 1-l beaker was filled with 24.5 g styrene–acrylic latex, 1.5 g P.B. 15:3 for cyan toner (C), 0.5 g P.Y. 151 for yellow toner (Y), 0.2 g P.R. 57:1 and 0.7 g of P.R. 122 for magenta toner (M), 3 g wax, and 120 g deionized water and the contents were mixed manually at room temperature for about 15 min. The resulting suspension was mixed using a Homogenizer for 5 min. The next step started with continuous mixing of ingredients at room temperature for about 1 h followed by the addition of a solution of 0.6 g coagulation agent in nitric acid over 10 min until the mixture reached a pH value of 2. In this manner, a gel was observed to form as a result of changing the viscoelastic nature of the suspension from a Newtonian water-like fluid to a shear thinning paste-like gel. The temperature of the mixture was raised to 50 °C for about 30 min while the gel was continually mixed. The mixture was held at this temperature for another 60 min. The temperature of the mixture was increased to 96 °C for 30 min, and held for a further 60 min. The ultimate mixture was neutralized with sodium hydroxide solution and cooled down to 25 °C, after which the produced particles were isolated from the water, washed to remove divalent ions, filtered, and dried with a frizzed dryer.

Employing CCD approach, we aimed at process optimization based upon two changing variables, namely mixing time and agitation speed, each at three levels. The highest and lowest values for the level of each factor are chosen based on previous works, as summarized in Table 1.

In this way, 13 sets of experiments were designed to explore the effects of the aforesaid parameters and colorants on various responding variables, including particle size (PS), particle size distribution (PSD), and colorimetric properties (L^*, a^*, b^*) of the toners produced. The corresponding design matrix is achieved by Expert-Design software and the process were optimized using thirteen experiments described within Table 2. The ANOVA and R^2 were used to check the adequacy of the developed model. A given mathematical model can be acceptable when its ANOVA reaches high statistical significance, with F-values at a level of confidence of 95% and P-values lesser than 0.05.

3.3. Characterization

The resultant color toners were centrifuged and dispersed in water, then sonicated for 2 min to break down aggregations. The dispersions were prepared for particle size and particle size distribution measurement using a particle size analyzer (PSA, Malvern Master sizer 2000, England) in the range of 0.02–2000 μm. Evaluation of the particle size distribution was done using the span parameter (Eq. (2)):

$$\text{Span} = \frac{(D90 - D10)}{D50} \quad (2)$$